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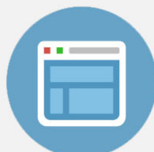

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Growth of pseudomorphic insulating HoF_3 layers on Si(111)

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We report the successful growth of pseudomorphic, trigonal structured HoF_3 insulating layers, stable at room temperature, on the Si(111) surface. Normally the tysonite structure is only stable at temperatures above 1070 °C [R. E. Thoma and G. D. Brunton, Sov. Phys. Crystallogr. **18**, 473 (1966)]. A phase transition to the lower-temperature orthorhombic structure is observed for a thickness of around 12 Å, consistent with the relaxation of elastic strain in the insulating layer.

There have been numerous reports of the growth of single-crystal fluoride insulating layers on semiconductors with most attention being paid to the alkaline earth difluorides on Si and GaAs. These fluorides can be mixed to yield a wide range of lattice constants enabling compositions to be chosen which may be lattice matched to the semiconductor. Unfortunately, however, there is a large difference in the thermal expansion coefficients of silicon[1] and the alkaline earth difluorides,[2] leading to cracking of the insulating layer upon cooling following growth at high temperature ($\sim$700 °C). The rare-earth trifluorides have smaller thermal expansion coefficient mismatches to the common semiconductors than the alkaline earth difluorides,[2] prompting studies of the growth of LaF_3 on Si(111) (Ref. 3) and on GaAs(111).[4] The rare-earth trifluorides have the additional advantage of being insoluble in water.[5] Unfortunately, the lattice mismatch between LaF_3 and silicon is large, around 8%, which is likely to lead to misfit dislocations for all but the thinnest of layers. LaF_3 has a trigonal structure[6,7] which is compatible with the Si(111) surface.

In this communication we report the growth of epitaxial layers of HoF_3 on Si(111) surfaces. In its normal room-temperature form HoF_3 has an orthorhombic structure[8] which is incompatible with the Si(111) surface in terms of symmetry. However, there exists another phase of HoF_3 which has a trigonal or tysonite structure[8] with a lattice parameter differing from that appropriate to the Si(111) surface by only 2.3%. Plan views of the orthorhombic and trigonal structures are shown in Fig. 1. Unfortunately the trigonal form of HoF_3 usually exists only at temperatures above 1070 °C. However, the possibility exists that thin layers of this structure might be stable at room temperature if grown on a suitable substrate. In this communication we report that this is indeed the case for growth on Si(111) surfaces.

HoF_3 was deposited onto clean Si(111) by evaporation from tungsten coil-type filaments located within a specially designed preparation chamber which was attached to a Vacuum Generators Ltd. ESCAlab mark II instrument and equipped with an *in situ* quartz crystal oscillator for thickness determination. Within the ESCAlab, low-energy electron diffraction (LEED) measurements could be recorded and x-ray photoelectron spectroscopy (XPS) data generated using MgK_α radiation and a concentric spherical sector analyzer.

Investigations of the Si 2s emission intensity (peak area) with increasing HoF_3 coverage are summarized in Fig. 2. The data points were established with the sample at room temperature, while each HoF_3 coverage was grown with the sample at 700 °C. The logarithmic decrease in the intensity for thicknesses below $\sim$12 Å, and the resulting derived free path of 22 Å for the Si 2s electrons traversing the insulating layer, shows that the HoF_3 grows in a layer-by-layer fashion for these coverages. For thicknesses greater than $\sim$12 Å, however, the behavior of the attenuation plot changes, reflecting a substantial degree of island growth.

The LEED investigations also show thickness-dependent behavior differing above and below $\sim$12 Å. For small coverages the Si(111)-(7×7) structure is replaced by one that resembles a Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$ pattern, shown in Fig. 3(a). This pattern is only observed for thicknesses below $\sim$12 Å and is very clearly reflecting a structure associated with the HoF_3 layer and not the substrate. For thicknesses greater than $\sim$12 Å a different LEED pattern, shown in Fig. 3(b), is observed. This pattern may be readily understood in terms of a triple-domain orthorhombic structure as illustrated in Fig. 4. Each domain is rotated by 120° with respect to the other. Detailed studies of the structures of thick layers by x-ray diffraction are entirely consistent with this view.

It is concluded, therefore, that thick HoF_3 layers on Si(111) possess an orthorhombic structure, and are composed of three domains, each rotated by 120° with respect to the other. Below a thickness of $\sim$12 Å, however, the growth is laminar and the LEED pattern resembles that of the Si(111)-($\sqrt{3} \times \sqrt{3}$)$R30°$. This pattern is in fact the same as that seen for layers of LaF_3 on GaAs(111) (Ref. 4) and on InP(111) (Ref. 9) which has only the trigonal structure, isomorphous with the mineral tysonite. Clearly, therefore, the LEED pattern observed for thicknesses below $\sim$12 Å reflects the structure of the trigonal form of HoF_3, and this pseudomorphic insulating layer has retained its naturally high-temperature form down to room temperature.

It is of interest to consider the phase transition for a thickness of 12 Å a little further. The growth of thin

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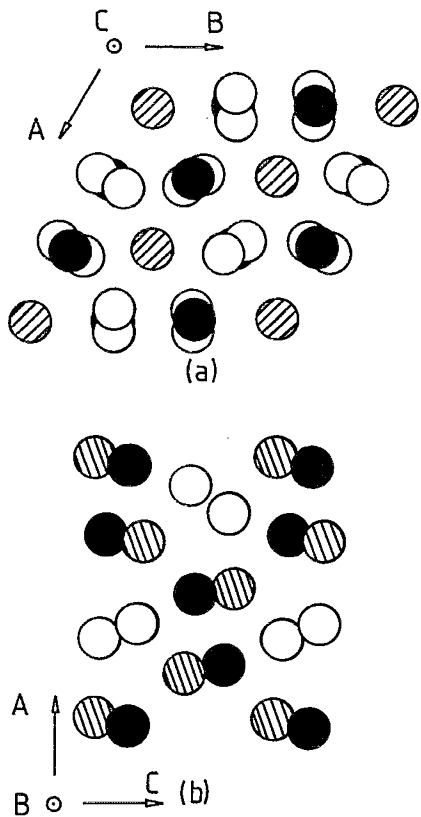


FIG. 1. (a) The trigonal structure of a rare-earth trifluoride (after Ref. 6). (b) The orthorhombic structure of a rare-earth trifluoride (after Ref. 8). ○ represents a F^- ion. ⊘ represents two F^- ions with one positioned on top of the other. ● represents a rare-earth ion.

pseudomorphic strained layers is now common and several theories have been put forward to account for the strain dependence of the critical thickness t_c, where the elastic strain can no longer be retained in the layer, leading to the onset of misfit dislocations. The mechanical model of Matthews and Blakeslee[10] has been particularly successful in describing the behavior of t_c for III-V and II-VI semiconductors. In this case a lattice mismatch of around 2% commonly leads to a value for t_c of around 30 Å. The mismatch of 2.3% between the Si(111) surface and the tysonite form of HoF_3 would thus be expected to lead to a critical thickness t_c of the order of the 12 Å observed in this work. However, in the absence of the relevant mechanical parameters for HoF_3 it is not possible to carry out a more accurate evaluation of t_c. The data thus strongly suggest that the transition from trigonal to orthorhombic growth at ~12 Å is associated with the relaxation of elastic strain in the HoF_3 overlayer.

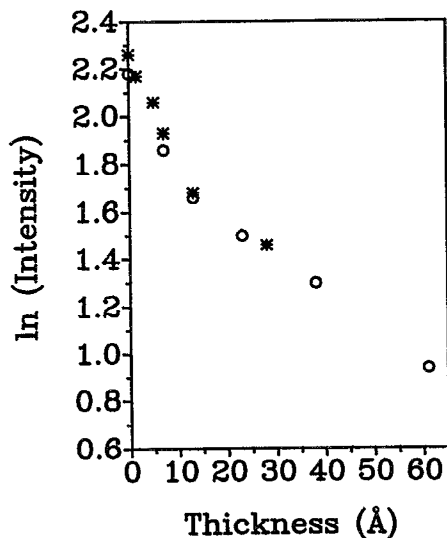
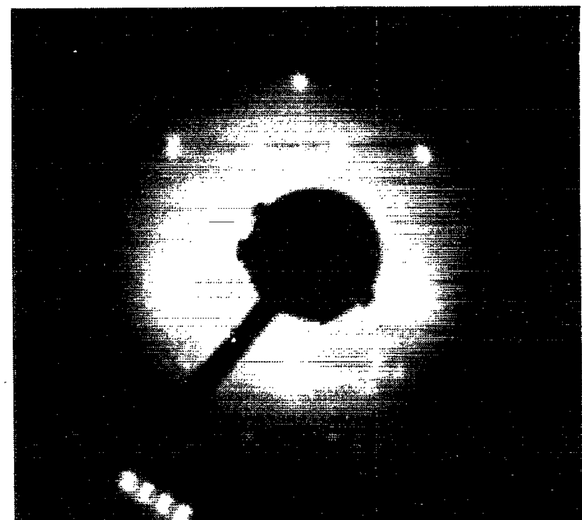
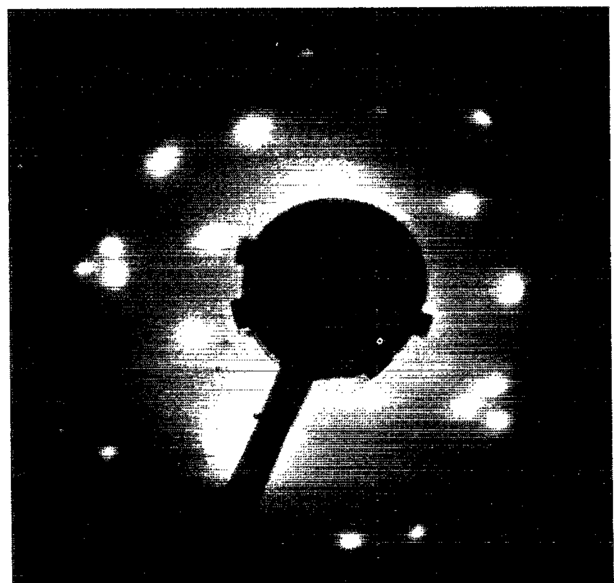


FIG. 2. Attenuation plot of the Si 2*s* XPS core-level intensity as a function of HoF_3 thickness. The two different symbols refer to data collected from two separate experiments.



(a)



(b)

FIG. 3 (a) A $(\sqrt{3}\times\sqrt{3})R30°$-like LEED pattern taken after 12 Å of HoF_3 had been deposited at 750 °C. Primary beam energy of 38 eV. (b) A triple-domain LEED pattern recorded after more than 12 Å of HoF_3 had been deposited at 700 °C. Primary beam energy of 36 eV.

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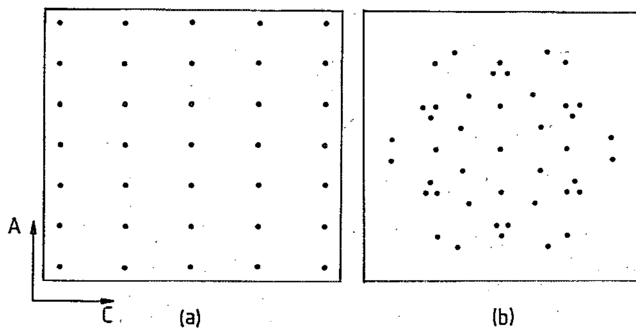

FIG. 4. (a) The reciprocal space mesh of orthorhombic HoF_3 (in the [010] direction). (b) The above mesh with an additional two components rotated by 120° and 240°, respectively. This reproduces the LEED pattern seen in Fig. 3(b).

In conclusion, we have shown that it is possible to grow a pseudomorphic epitaxial insulating layer of HoF_3 on Si(111). As far as we can ascertain, this is the first observation of the growth of an insulating layer on Si where the phase normally only stable at high temperatures can be retained at room temperatures. Clearly, therefore, in exploring suitable insulating fluoride layers on semiconductors, it is essential to consider all known structures of those materials, and not just the structure which is stable at room temperature.

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